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Abstract of **JP5110139**

PURPOSE:To improve the crystallizability of a laminated crystal by growing GaN films and AlN films alternately and separately and as multilayer film layers in such manner that GaXAl1-XN seems to grown, and by stopping the lattice defect of gallium nitride compound to be grown on a sapphire substrate.

CONSTITUTION:In the crystal growth method of gallium-aluminum nitride represented by general formula GaXAl1-XN (0<X<1), multilayer film layers, in which thin-film GaN layers and thin-film AlN layers are grown alternately, are grown; and further the GaN layers and AlN layers of the multilayer film layers are grown so that the ratio of the total film thicknesses of respective GaN layers and AlN layers corresponds to the molar ratio of gallium-aluminum nitride. A large distortion is generated by the difference in lattice constant between sapphire substrate and GaN layers. Further, a lattice defect is generated in the GaN layers by this distortion. When different thin-film materials are laminated on the way, the continuously generated defect can be stopped at that place.

[Claim(s)]

[Claim 1] It is the crystal growth approach of a gallium nitride aluminum semi-conductor that a general formula is expressed with GaXAl1-XN (0< X<1). As the multilayers layer into which the GaN layer of a thin film and the AlN layer of a thin film were grown up by turns is grown up and the ratio of each total thickness of the GaN layer of the multilayers layer and an AlN layer supports the mole ratio of said gallium nitride aluminum semi-conductor further The crystal growth approach of the gallium nitride aluminum semi-conductor characterized by growing up a GaN layer and an AlN layer.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the crystal growth approach of the gallium nitride aluminum semi-conductor which is applied to the crystal growth approach of a gallium nitride aluminum semi-conductor that a general formula is expressed with GaXAl1-XN (0< X<1), especially is used for luminescence devices, such as a blue light emitting diode and a blue laser diode.

[0002]

[Description of the Prior Art] Research is advanced using an II-VI group's ZnSe, an IV-IV group's SiC, an III-V group's GaN, etc., it is announced that luminescence in which the gallium nitride system compound semiconductor [GaXAl1-XN (however, 0<=X<=1)] was comparatively excellent also in it with ordinary temperature is shown recently, and the blue luminescence device attracts attention. The blue luminescence device is obtained by growing up fundamentally into n mold, i mold, or p mold the crystal of the gallium nitride system compound semiconductor (unless it is required especially the following, the phrase of a semi-conductor is omitted.) by which a general formula is expressed with GaXAl1-XN (however, 0<=X<=1) on silicon on sapphire generally, and carrying out the laminating of them.

[0003] As an approach of growing up the crystal of a gallium nitride system compound, vapor growth, such as organometallic compound vapor growth (henceforth the MOCVD method) and a molecular beam epitaxy method (henceforth the MBE method), is known well. When the approach using the MOCVD method is explained briefly, for example, this approach In the reaction container which installed silicon on sapphire, as reactant gas Organometallic compound gas {trimethylgallium (TMG), Supply}, such as trimethylaluminum (TMA) and ammonia, and crystal growth temperature is held to an about 900 degrees C - 1100 degrees C elevated temperature. It is the approach of carrying out the laminating of the gallium nitride system compound to n mold, i mold, or p mold, growing up the epitaxial layer of a gallium nitride system compound, and supplying other reactant gas if needed on a substrate. Although there are sapphire, SiC, Si, etc. in a substrate, generally sapphire is used.

[0004] however, MOCVD -- law and MBE -- the brightness is low and the blue luminescence device using the blue light emitting device obtained by vapor growth, such as law, for example, blue light emitting diode, has not yet resulted in utilization. because, the gallium nitride system compound which grows on silicon on sapphire conventionally -- the most -- GaN -- it is -- the GaN -- several sorts of impurities -- doping -- an n mold GaN layer -- high -- it is because the laminating of the i mold GaN layer [****] is carried out and light is made to emit by the junction of n layers and i layers. Moreover, this invention person showed that the p mold GaN was realizable by

growing up GaN as a buffer layer in Japanese Patent Application No. No. 89840 [three to] first.

[0005]

[Problem(s) to be Solved by the Invention] In order to put in practical use raise in the brightness of light emitting diode, or blue laser diode which has not yet been realized, it is necessary to consider as the p-n junction of the double hetero structure which the crystal of not only the p-n junction of GaN(s) but the gallium nitride aluminum of GaAlN is grown up, makes GaAlN a cladding layer, and makes GaN a barrier layer, or single hetero structure. In order to realize this, it is necessary to grow up the crystal of n mold of high quality, or the p mold GaAlN.

[0006] MOCVD when growing up the crystal of GaAlN by vapor growth conventionally -- in law, the mixed-crystal film was grown up by mixing according to the mole ratio of Ga and aluminum TMG gas and TMA gas want to grow up to be in a reaction container, or adjusting a quantity of gas flow. Moreover, in the MBE method, into the reaction chamber, Ga atom and aluminum atom were made to live together, and it was growing up similarly. However, by the approach of mixing gas etc. like before and carrying out vapor growth at once, the crystallinity got extremely bad compared with growing up a GaN independent, and the crystal of high quality was not obtained as AlN increased in mixed-crystal when X of GaXAl1-XN was made small namely. Since the mixed-crystal film of the p mold GaAlN was not obtained by not acquiring the outstanding crystallinity, naturally implementation of the light emitting diode of said single hetero and double hetero structure, laser diode, etc. was impossible.

[0007] It is in the place which accomplishes this invention in view of such a situation, and is made into the purpose realizing light emitting diode of a single hetero and double hetero structure, and laser diode by offering the crystal growth approach by which the mixed-crystal film of gallium nitride aluminum excellent in crystallinity is obtained.

[0008]

[Means for Solving the Problem] this invention person -- a silicon-on-sapphire top -- MOCVD -- when the gallium nitride aluminum crystal was grown up on condition that many using law, that it is alike, and follow and the crystallinity worsens [to which the mole ratio of aluminum of GaXAl1-XN becomes large] thought that they interfered, there were and crystallinity worsened by passing the gas (here TMG, TMA, ammonia) used as a raw material to coincidence. Then, when using as the thin film layer the film into which it grows up to be separately by turns, and the GaN film and the AlN film are moreover grown up, respectively in order to pass gas separately, and seeing macroscopically, things are found out that it can be whether GaXAl1-XN is growing, and

it came to accomplish this invention.

[0009] The crystal growth approach of this invention is the crystal growth approach of gallium nitride aluminum that a general formula is expressed with GaXAl1-XN (0< X<1). As the multilayers layer into which the GaN layer of a thin film and the AlN layer of a thin film were grown up by turns is grown up and the ratio of each total thickness of the GaN layer of the multilayers layer and an AlN layer supports the mole ratio of said gallium nitride aluminum further It is characterized by growing up the GaN layer and AlN layer. Namely, it faces that this invention grows up the gallium nitride aluminum crystal by which a general formula is expressed with GaXAl1-XN (0< X<1). Make an atom etc. intermingled in a reaction container in organic metal gas or the MBE method in the MOCVD method like before, and it does not grow up at once. The GaN layer and AlN layer of a thin film are grown up by turns, and each layer is grown up so that the ratio of the sum total of the thickness of each layer may correspond to mole ratio X of GaXAl1-XN, and 1-X.

[0010] The case where a gallium nitride system compound is grown up is explained as double hetero structure which makes a cladding layer an n mold GaAlN layer and a p mold GaAlN layer for the crystal growth approach of this invention in C side of silicon on sapphire for example, using the MOCVD method, and makes a p mold GaN layer a barrier layer. First, the silicon on sapphire washed beforehand is installed in the susceptor in a reaction container, among reducing atmosphere, a susceptor is heated at 1000 degrees C or more by high-frequency heating etc., and the oxide on a substrate is removed. After cooling slowly and lowering the temperature of a susceptor even before and after 600 degrees C after heating, reactant gas is supplied in a reaction container and the buffer layer of GaXAl1-XN (however, 0<=X<=1) is first grown up on a substrate. Reactant gas uses ammonia gas as organometallic compound gas, such as TMA, and a source of N as TMG and a source of aluminum as a source of Ga. After growing up a buffer layer, temperature of a susceptor is made into an elevated temperature 900 degrees C or more, it holds at 1050 degrees C, and TMG gas and ammonia gas grow up the crystal of GaN with a sink. In obtaining the GaN layer of n mold, it usually dopes Si for silane gas during a sink GaN crystal with those gas.

[0011] Then, when growing up the crystal layer of n mold Ga0.3aluminum0.7N on it, holding at 1050 degrees C, the about ten-layer laminating of the thin film of GaN and AlN is carried out for TMG gas and TMA gas with a sink by turns, and the crystal of a multilayers layer is grown up. Although the laminating of the crystal of the GaN film and the AlN film is carried out to this multilayers layer by turns, it grows up so that the sum total of each thickness may be set to GaN:AlN=3:7. The ratio of a TMG quantity of

gas flow and a TMA quantity of gas flow may be set to 3:7, and may be grown up into it, and by changing the time amount which passes gas, thickness may be adjusted and may be grown up.

[0012] Then, in order to form a p mold GaN layer on an n mold Ga0.3aluminum0.7N layer, in addition to TMG gas, diethyl zinc (DEZ), magnesium cyclopentadienyl (Cp2Mg) gas, etc. are passed, and Zn or Mg which is p mold impurity is doped in a GaN layer. When growing up p mold Ga0.3aluminum0.7N on it furthermore, a multilayers layer can be grown up like the above-mentioned. In order to use a multilayers layer as p mold, in addition, passing the gas of Zn or the source of Mg is continued also during growth. Thus, the sectional view of the component which has the obtained gallium nitride system compound is shown in drawing 1 . This component is made into the double hetero structure which makes a cladding layer an n mold Ga0.3aluminum0.7N layer and a p mold Ga0.3aluminum0.7N layer, and makes a p mold GaN layer a barrier layer.

[0013] As for the buffer layer first grown up on silicon on sapphire, in the crystal growth approach of this invention, it is more desirable to make it grow up, in order to raise the crystallinity of the gallium nitride system compound to be grown up from now on. Although the general formula can be expressed with GaXAl1-XN (0<=X<=1), GaAlN is made into a buffer layer and the buffer layer of GaN is [crystallinity is / direction / desirable and] the most desirable rather than it makes AlN into a buffer layer, as this invention person clarified before. The growth temperature of a buffer layer is usually 200 degrees C - 900 degrees C low temperature. for example, MOCVD -- although it is around 500 degrees C in law -- MBE -- it can be made to grow up at the temperature not more than it by law

[0014] The growth temperature of a multilayers layer can be formed at the same temperature as the temperature at the time of growing up a gallium nitride system compound. Moreover, the laminating of a GaN layer and the AlN layer is carried out more than two-layer by 10-3000A thickness, respectively, and they usually carry out a 10-100-layer laminating by the thickness around 20-500A. When it is difficult to stop the lattice defect described later if the total thickness of multilayers is thinner than 20A and each thickness is larger than 3000A, it is in the inclination for the crystallinity of the multilayers layer to worsen.

[0015]

[Function] The multilayers layer of this invention can be whether GaXAl1-XN is growing by growing up the GaN film and the AlN film separately by turns, as described above, and growing up as a multilayers layer. Moreover, the lattice defect of the gallium nitride system compound which grows on silicon on sapphire by this multilayers layer

as other operations can be stopped. As for silicon on sapphire (C side) and GaN, the lattice constant has shifted about 16%. The gap is still larger if it results in AlN. A big distortion occurs between silicon on sapphire and a GaN layer by the difference in this lattice constant. Furthermore, a lattice defect is made by this distortion into a GaN layer, and this defect runs continuously to the last during GaN growth. For this reason, the multilayers layer of this invention has the operation which can be stopped here by carrying out the laminating of the thin film material which is different on the way in this defect made continuously.

[0016]

[Example] The crystal growth approach of this invention is explained in full detail in the example below.

[Example 1]

** Install the silicon on sapphire washed well first in the susceptor in a reaction container. After carrying out evacuation of the inside of a container, the substrate was heated for hydrogen gas for 20 minutes at 1050 degrees C with the sink, and the surface oxide was removed. Then, temperature was cooled even at 500 degrees C, it considered as the source of Ga in 500 degrees C, and the GaN buffer layer was grown up by 200A thickness with the sink in hydrogen gas as ammonia gas and carrier gas as TMG gas and a source of N.

[0017] ** After raising only TMG gas next and raising a stop and temperature even at 1030 degrees C, the sink and the Si dope n mold GaN layer were again grown up by 4-micrometer thickness in TMG gas and SiH4 (mono silane) gas.

[0018] ** next, TMA gas after TMA gas grew up [TMG gas] 20A of sink AlN layers as a stop and a source of aluminum -- a stop -- similarly TMG gas grew up 80A of sink GaN layers by 4 times as much time amount as TMA gas again. This actuation was repeated 15 times by turns, and the multilayers layer of Si dope which consists of 30 layers of AlN layers of 20A of thickness and 30 layers of GaN layers of 80A of thickness was grown up. That is, about the gallium nitride aluminum mixed-crystal layer of n mold Ga0.8aluminum0.2N, I hear that 3000A grew and it is.

[0019] ** SiH4 gas and AlN gas were stopped and Cp2Mg gas newly grew up the Mg dope p mold GaN layer by the thickness of 0.5 micrometers on the polycrystal membrane layer succeedingly with the sink.

[0020] ** Succeedingly, carrying out the laminating of the GaN film and the AlN film for Cp2Mg gas on a sink and a p mold GaN layer, like **, instead of SiH4 gas, 3000A grew the gallium nitride aluminum mixed-crystal layer of p mold Ga0.8aluminum0.2N, and the component which has a gallium nitride system compound was produced by forming

a multilayers layer.

[0021] [Example 1 of a comparison] In ** and **, by setting the mole ratio of TMG gas and TMA gas to 8:2, and passing in a reaction container to coincidence, the mixed-crystal film of n mold Ga0.8aluminum0.2N and p mold Ga0.8aluminum0.2N was formed by 3000A thickness, respectively, and also the gallium nitride system compound component was produced like the example 1.

[0022] Thus, the following trials were performed in order to evaluate the crystallinity of a gallium nitride aluminum crystal of the component of the example 1 and the example 1 of a comparison which were acquired.

[0023] First, the p mold Ga0.8aluminum0.2N layer double crystal X-ray rocking curve was measured, and it asked for the half-value width (FWHM:full width at half-maximum). It can be considered that the crystallinity is excellent, so that FWHM is small. Consequently, it of the example of a comparison was 7 minutes to p type layer of an example 1 having been 3 minutes.

[0024] Next, when p mold Ga0.8aluminum0.2N layer hole carrier concentration was measured by hole measurement, to it of an example 1 having been 1x1018-/cm3, it of the example of a comparison is high resistance, and was not able to be measured. this shows that the crystallinity of the gallium nitride aluminum by the approach of this invention is markedly alike, and excellent.

[0025] Furthermore, after making the obtained component the chip of 0.5mm angle by dicing, blue light emitting diode (LED) was produced and was made to emit light by taking out an electrode from p type layer and n type layer, setting to a leadframe according to a conventional method, and giving resin mold. Consequently, in 20mA of forward current, it did not pass over LED of the example 1 of a comparison to 20 microwatts to LED obtained from the component of an example 1 having been 150 microwatts of 430nm radiant power outputs. Moreover, it of the example of a comparison was 30V to the forward voltage of LED of an example 1 having been 4V.

[0026] [Example 2] In the process of ** and **, the component which carry out the laminating of 40A of AlN layers and every 20 layers of the GaN layers by turns by 160A thickness, and it considers as the mixed-crystal film of n mold Ga0.8aluminum0.2N and p mold Ga0.8aluminum0.2N, respectively, and also has the crystal of a gallium nitride system compound like an example 1 was obtained.

[0027] When this component as well as FWHM measurement, hole measurement, and blue light emitting diode performed crystalline evaluation, the almost same result as the component obtained in the example 1 was obtained.

[0028] [Example 3] In the process of ** and **, a 20A AlN layer for the multilayers layer

to grow up Ten layers, Ten layers and a 240A GaN layer for ten layers and a 80A GaN layer Ten layers, [a 60A AlN layer] The laminating of a GaN layer and the AlN layer was carried out at random by turns, changing each thickness, and the mixed-crystal film of Ga0.8aluminum0.2N and p mold Ga0.8aluminum0.2N whose total thickness is 4000A was grown up. Others obtained the component which has the crystal of a gallium nitride system compound like an example 1.

[0029] When this component as well as FWHM measurement, hole measurement, and blue light emitting diode performed crystalline evaluation, the almost same result as the component obtained in the example 1 was obtained.

[0030] [Example 4] In the process of ** and **, the component which carry out the laminating of an AlN layer and every ten layers of the GaN layers by 50A thickness, respectively, and it considers as the mixed-crystal film of n mold Ga0.5aluminum0.5N and p mold Ga0.5aluminum0.5N, respectively, and also has the crystal of a gallium nitride system compound like an example 1 was obtained.

[0031] When this component as well as FWHM measurement, hole measurement, and blue light emitting diode performed crystalline evaluation, the almost same result as the component obtained in the example 1 was obtained.

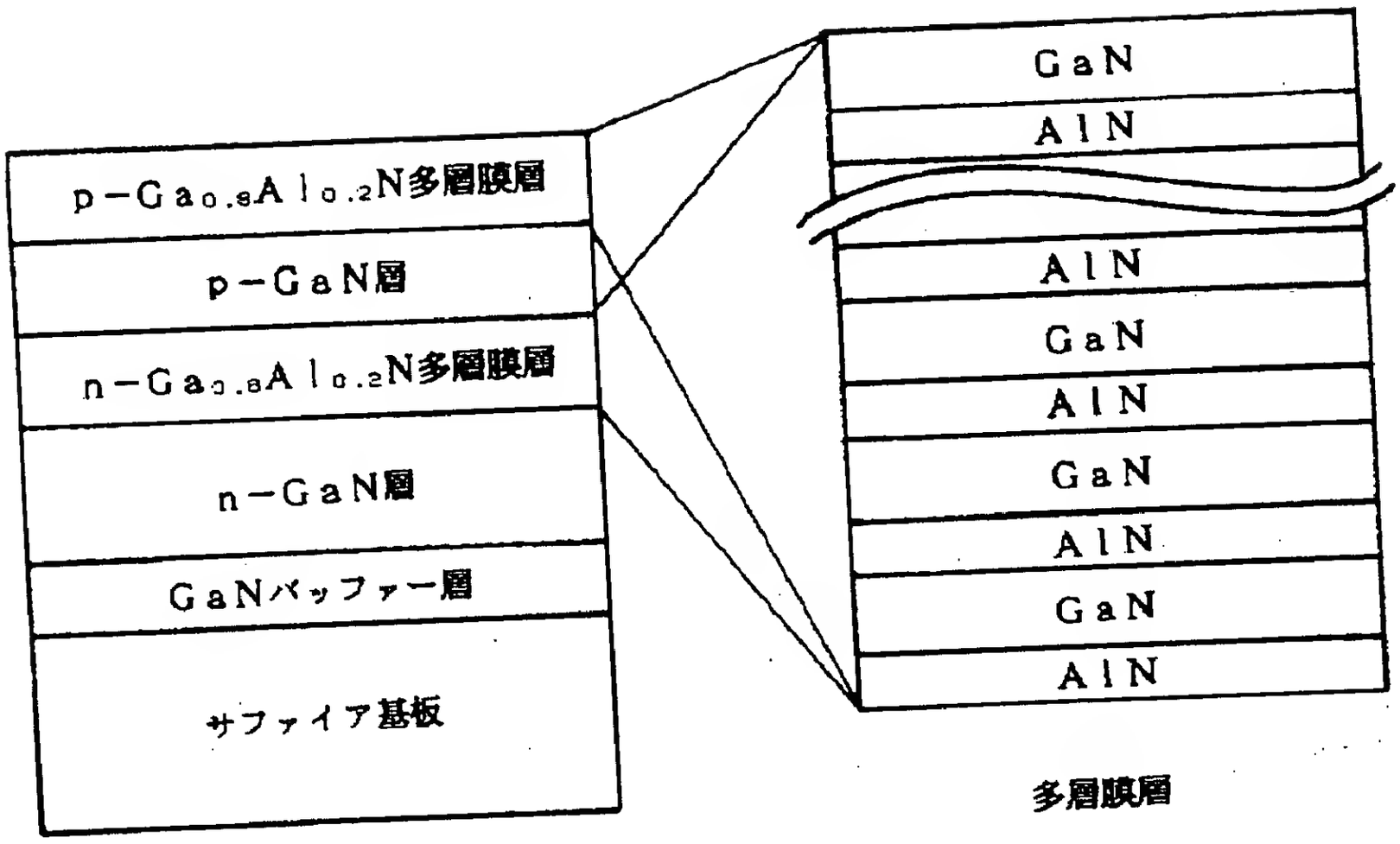
[0032]

[Effect of the Invention] As explained above, the crystal growth approach of the gallium nitride aluminum of this invention can be whether GaXAl1-XN is growing by growing up the GaN film and the AlN film separately by turns, and growing up as a multilayers layer. moreover, since the lattice defect of the gallium nitride system compound grown up on silicon on sapphire can be stopped, the crystallinity of the crystal which carried out the laminating can be boiled markedly, and can be raised. since it can be made as terrorism structure to double and the component which carried out the laminating of the gallium nitride system compound impossible further conventionally can be made into terrorism structure to a single -- high -- a brightness light emitting diode, a laser diode, etc. can be realized, and a great thing has a merit on industry towards utilization of a blue luminescence device etc.

[Brief Description of the Drawings]

[Drawing 1] The mimetic diagram showing the cross section of the component by one example of the crystal growth approach of this invention.

[Drawing 1]


p−Ga0.8Al0.2N多層膜層
p−GaN層
n−Ga0.8Al0.2N多層膜層
n−GaN層
GaNバッファー層
サファイア基板
GaN
AlN
AlN
GaN
AlN
GaN
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GaN
AlN
多層膜層